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Testing and modification of experimental procedures has occupied the bulk of the project's first year. Methods investigated include quantitative x-ray diffraction analysis and differential scanning calorimetry to monitor calcium hydroxide solid phases, XRD and infrared spectroscopy to investigate clay mineral degradation, and ion chromatography of pore solution.

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OF CEMENT PASTE BY INCORPORATION OF ALUMINOSILICATE CLAYS: EFFECT
ON STRENGTH, DURABILITY, AND TOUGHNESS
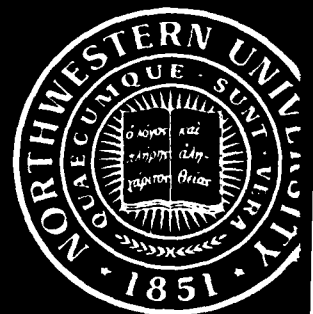
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Annual Report

Technological Institute
NORTHWESTERN UNIVERSITY
EVANSTON, ILLINOIS

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Annual Report

Submitted to

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ABSTRACT

This report describes the theoretical basis, experimental approaches, and results to date of research carried out to determine whether addition of natural aluminosilicate clays to Portland cement can improve mechanical properties of hardened pastes. The concept that such additions hold promise for stronger and tougher cement-based composites stems from the physicochemical properties of these clays including, for example, high specific surface compared to silica fume, ion-exchange behavior, needle-like crystal morphology in certain cases, and particle sizes in the colloidal range. These characteristics tend to allow reduction of pore sizes in porous media, increases in Van der Waals bonding of solid phases in composites, and manipulation of chemical composition of pore solutions.

Testing and modification of experimental procedures have occupied the bulk of the project's first year. Methods investigated include quantitative x-ray diffraction analysis and differential scanning calorimetry to monitor calcium hydroxide solid phases, XRD and infrared spectroscopy to investigate clay mineral degradation, and ion chromatography of pore solutions.

ACKNOWLEDGEMENTS

INTRODUCTION

Overall Objectives

The primary objectives of the work are to determine whether addition of the appropriate types and amounts of alumino-silicate clays to hydraulic cement pastes and concrete mixtures can increase strength, durability, and toughness of the materials, and to understand the major physico-chemical mechanisms that govern properties of the cement-clay mixtures. Coupled with these are consequent objectives, i.e., to determine to what extent undesirable properties are imparted to cement pastes and concrete by addition of clays, and to determine what pretreatments of the clays will be necessary for optimum effectiveness.

Technical Background

High-strength cement pastes and composites have generally been obtained by reducing porosity and pore sizes. One approach to achieving such reductions is through the addition of fine particles into the cement-based mixtures such that spaces between hydration products and/or aggregates are filled. For example, the addition of condensed silica fume (microsilica), with particle sizes on the order of 5 nm to 0.5 nm, increases compressive strength to around 300 MPa (about 43,000 psi) (Young, 1985). The use of condensed silica fume, however, tends to increase brittleness. In another study, the addition of colloidal alumina has been shown to markedly increase the tensile strength of cement paste compounds through hot-pressing (Oyefesobi and Roy, 1977).

These observed effects are not entirely unexpected -- in addition to decreasing pore sizes and porosity, fine particles have large specific surface areas, which would allow increased bonding between particles by Van der Waals attractive forces, leading to increased strength of the material. It is well known that these attractive Van der Waals forces between crystals of cement

4

hydration products provide the principal source of strength in hydrated cement paste. These are the same forces that cause adhesion of cement hydration products to clinker grains and aggregates. Thus, it can be inferred that incorporation of fine colloidal phases, with higher specific surface areas than microsilica, could possibly result in cement pastes and concrete with higher strengths than are now obtained with the microsilica.

On the basis of this hypothesis, it was proposed to test the effectiveness of colloidal aluminosilicate clays as additives to increase strength of cement paste mixtures. It was also hypothesized that additions of such clays would impart other improvements in the properties of cement-based composites. The arguments that support these hypotheses are as follows:

1. The alumino-silicate clays have large specific surface areas; for example, surface areas as measured by N_2 adsorption are on the order of 10-30 m^2/g for kaolinites, 40-100 m^2/g for montomorillonites, 70-120 m^2/g for illites (hydrous micas), 360 m^2/g for laponite, and 50-83 m^2/g for attapulgite (Van Olphen, 1977; Van Olphen and Fripiat, 1979; Bohn et al., 1985). In comparison, microsilica has surface areas in the range of 20-25 m^2/g.

2. Alumino-silicate clays tend to be platy, with the basal planes generally being the largest dimension. Thus, a certain degree of flexibility may be imparted to the cement paste and concrete by the platy clays than is afforded by more spherical particles such as condensed silica fume. The clay mineral attapulgite tends to occur as long needles, and may reduce brittleness in a manner similar to the effect of steel, glass or asbestos fibers (Shah, 1986) but probably not to the same extent.

3. Alumino-silicate clays can be prepared with a preferred cation as counterion. The clays tend to possess a net negative electrostatic surface

5

charge due mainly to isomorphic substitution within the clay lattice of Al for Si in the tetrahedral layer, and Mg for Al in the octahedral layer. Cations will bind to such clays and tend to be exchanged for other cations in the surrounding solution. Thus, clay additives to cement and concrete could be prepared such that the counterion can be a cation that may impart desirable properties to the mixture. For example, if the counterion is H^+, the latter can exchange for Ca^{+2} in the hydrating mixture, neutralizing some of the alkalinity caused by the $Ca(OH)_2$ forming in the transition zone, as illustrated by the schematic reaction

$$clay \, \begin{matrix} H^+ \\ H^+ \end{matrix} + Ca(OH)_2 = clay \, Ca^{+2} + 2HOH$$
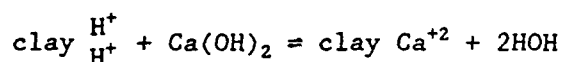
This neutralizing action would reduce the tendency for large crystals of $Ca(OH)_2$ to form, which possess less surface area and thus weaker Van der Waals attractive force; $Ca(OH)_2$ also tends to provide cleavage sites for the hardened pastes due to their orientation. Also, if Na^+ is present in the cement paste, formation of NaOH with its detrimental effects on silica would be minimized with neutralization of the hydroxyl ion. One complication to this process is the fact that H^+-saturated clays tend to be unstable, i.e., H^+ tends to enter the clay lattice and release Al^{+3} onto the exchange site so that a clay freshly prepared as an H-clay eventually becomes an Al-clay. The Al-clay would still tend to exhibit $Ca(OH)_2$ neutralizing power, but its ultimate effect on the cement paste due to formation of $Al(OH)_3$ needs investigation in relation to the formation of ettringite in the paste. A comment on this question by Paul Brown of the National Bureau of Standards, indicated that formation of ettringite under these circumstances will probably be unimportant due to the low concentration of free sulfate ion.

6

Clays prepared with Na^+ as one of the counterions could provide stability to the colloids in suspension during hydration, due to the large hydration shell of the sodium ion; however, the proportion of Na^+ as counterion would have to be carefully controlled, since too much Na^+ would (a) tend to flocculate the colloids, and (b) increase the concentration of Na in the hydration mixture, leading to alkali attack on the material. Addition of polyelectrolytes (hydrophilic colloids) may provide stability for the colloidal suspension during hydration, without addition of the undesirable Na ion.

4.   Addition of H-clays (or Al-clays) may tend to improve durability of cement paste by decreasing permeability and reducing the $Ca(OH)_2$ concentration in the hydrated material.

On the other hand, undesirable effects can be postulated for the use of alumino-silicate clays as additives, primarily due to adsorption of water. This latter property is particularly marked in the case of expanding-lattice clays such as the montmorillonites. The undesirable effects related to increased adsorption of water include shrinking, swelling, and creep. However, if the proportion of added clay is small, and the clay is pretreated appropriately, adverse effects may be tolerable in exchange for increased strength, ductility, and durability. More importantly, the use of non-expanding clays such as attapulgite would, theoretically, reduce the magnitude of water adsorption.

It was also proposed that a major effort throughout the work would be to obtain some understanding of the basic physicochemical reactions taking place in the mixtures as a consequence of the addition of the clays. The clays present competitive sites for ion adsorption and thus to some extent can affect ionic activities in the aqueous phase of the hydrating mixture. In turn, the

7

physicochemical behavior of the clays will tend to be affected by the pH of the suspending medium.

Objectives for the First Year

1. Feasibility testing

A major objective of the first year's work was to determine whether the concept of increasing cement-based materials strength by addition of aluminosilicate clays is a valid and feasible concept. Therefore, experimental work during the project's first year was focused on a wide range of materials and mixture compositions; these feasibility studies would subsequently define which clays and treatment methods should be investigated in further detail.

2. Selection and characterization of aluminosilicate clays

Aluminosilicate clays are natural materials that result from weathering of primary minerals in rock. Consequently, there is an almost infinite variety of these clays, depending on geologic origin of the rock, geographical location, and weathering history. Generally, however, there are about five major groupings that can be delineated. Of these five, three were selected for study and represent a wide range of properties pertinent to the objectives of this work: (1) Non-expanding, 1:1 lattice clays; (2) Expanding, 2:1 lattice clays; and (3) Non-expanding 2:1 lattice clays. Representative clay minerals of each of these groups were chosen, based on commercial availability of bulk quantities, since bulk quantities will be necessary if widespread use of these clays as additives will be recommended as a result of this work. The specific minerals selected for this study were kaolinite, bentonite, and attapulgite (palygorskite). Physicochemical characteristics of these materials are described in the MATERIALS section.

8

3.   Development of Methods

A number of physical, chemical, and mechanical testing methods are commonly used to characterize cement pastes, pore solutions, clay minerals, and associated components. One objective of the first year of study was to determine which of these methods would provide the information relevant to the overall objectives of the study, and what method modification, if any, would be needed in specific cases. These are described in the METHODS section.

MATERIALS

Clay Minerals

Kaolinite clay minerals are 1:1 lattice clays, i.e., each unit lattice consists of an octahedral layer of aluminum oxides and a tetrahedral layer of silicon oxides, with isomorphic substitutions in either or both layers such that the lattice has usually a net negative charge on its basal plane surface, depending on solution pH. The unit lattices are layered on each other, bound rather tightly with hydrogen bonds and thus the lattices do not expand upon wetting. A general stoichiometric formula for these minerals is $Al_4Si_4O_{10}(OH)_8$. The bulk material for use in this study was obtained from Georgia Kaolin Company.

Bentonitic clays (also referred to as montmorillonitic clays or smectites) are 2:1 lattice clays, i.e., each unit lattice consists of two silica tetrahedral layers and one alumina octahedral layer. The unit lattices are layered on one another, similar to the kaolinitic clays, except that the units are not bonded tightly and allow molecules of water and hydrated ions to penetrate between the layers, i.e., the layers expand when wetted, and contract when dryed. Because of the ability to adsorb ions between lattice layers, bentonitic clays have large specific surface areas relative to kaolinitic clays. Isomorphic substitution in the octahedral layers generally result in a net negative charge of bentonitic clays except at pH values less than about 2. A general stoichiometric formula for these minerals is $(Al_{3.15}Mg_{0.85})(Si_{8.00})(OH)_4X_{0.85}nH_2O$, where x $-$ monovalent interlayer cation. Bentonite for feasibility tests was obtained from Sargent Welch Chemical Company, as Wyoming Bentonite.

Attapulgite (also known more generally as palygorskite) is a 2:1 lattice clay, but does not expand. It thus has a specific surface area generally between that of kaolinite and that of bentonite. The non-expanding lattice along with

10

the needle-like morphology of attapulgite (Fig.1) render this type of clay the most promising in terms of improved cement composite properties. Attapulgite is used extensively in drilling muds in the oil industry. Approximate stoichiometric formula is $(OH_2)_4(OH)_2Mg_5Si_8O_{20} \cdot 4H_2O$.

Portland Cement

A type I Portland cement obtained from the Materials Services Corporation in Chicago, was used in all experiments.

Chemical characterization of these materials is continuing; some surface properties are listed in Table 1.

Figure 1. Brightfield Photomicrograph of 04 Attapulgite (figure taken
from Van Olphen and Fripiat, 1979).

Table I: SURFACE PROPERTIES OF EXPERIMENTAL MATERIALS

Material	C.E.C[1] m.e./100g	Exchangeable Cations (m.e./100g)[2]					Surface Area[3]
		Calcium	Magnesium	Sodium	Potassium	Aluminum[4]	m^2/g
Kaolinite	6.0	1.3	0.4	1.7	0.4	0.2	17.66
Bentonite	75.4	25.9	21.2	39.7	1.2	0.2	36.72[5]
Attapulgite 1	58.0	24.7	8.6	45.0	0.8	0.2	30.62
Attapulgite 2	56.8	22.0	9.9	43.5	1.0	1.3	
Portland Cement		--------Not Applicable---------					5.28

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[1] Cation Exchange Capacity, as milliequivalents per 100 grams air-dry clay, determined with 1M Ammonium Acetate, pH 7.

[2] As milliequivalents per 100 grams air-dry clay, determined on ammonium acetate extract at pH 7, using atomic absorption spectophotometry (Hitachi Zeeman Model 80).

[3] Based on linear portion of B.E.T. Plot as determined by N_2 adsorption (P/Po = 0.006 - 0.3) using OMNISORP 360.

[4] Due to the uncertainty in aluminum analysis by flame atomic absorption, these values will be checked by ion chromatography when the appropriate column is selected.

[5] External surface only, (N_2 adsorption does not measure internal surface of expansible clays).

METHODS

Methods used to characterize the individual clays are outlined in the footnotes to Table I, above. Other methods used during the project's first year are briefly described below. In this report, the term "original clays" refers to the clay material as received; the term "pre-treated clays" refers to clay material that was treated chemically (e.g., original counterions replaced with a different counterion,) or physically (e.g., pulverization and/or sieving), or both.

Calcium Hydroxide Quantitation

Monitoring of the quantity and formation rate of $Ca(OH)_{2(s)}$ is essential to the objectives of this project. The traditional method of lime extraction with glycol or alcohol glycerol tends to give high values due to inclusion of CaO from other mineral phases in the hydrating mixture (Pressler et al., 1961; Midgley, 1979). X-ray diffraction has at least one major disadvantage, i.e., amorphous forms of $Ca(OH)_{2(s)}$ are not detected. Freshly forming solid phases do not necessarily exhibit crystallinity; only upon ageing does crystal structure manifest itself. Thus, a method that would identify $Ca(OH)_{2(s)}$ in non-crystalline form is needed to supplement quantitative x-ray diffraction. Differential scanning calorimetry is one such method that may have application here. This method is based on the measurement of endothermal peak areas obtained from thermal decomposition of $Ca(OH)_{2(s)}$ to $CaO+H_2O$. Possible limitations of the method include identification of the temperature intervals corresponding to calcium hydroxide decomposition, and interferences from other phases that may also decompose at similar temperature. The method has been applied favorably to studies with set Portland cements and with calcium silicate mixtures (Midgley, 1979; Ramachandran, 1979).

<u>Quantitative x-ray diffraction</u> (QXRD) as developed by Alexander and Klug (1948) and described for calcium hydroxide and calcium silicates by Copeland and Bragg (1958) were used in the first year of the project to characterize cement-clay hydrating mixtures. The instrument used was a Rigaku Dmax Series with integrated count (Cu Kα radiation). Sample holder is an aluminum plate 50 x 35 mm, with opening of 20 x 20 mm. The sample holder is placed on a glass slide and the hole filled with powder sample and compacted. Samples were ground in an agate mortar to pass a 45 μ stainless steel sieve. QXRD of calcium hydroxide and calcium silicate materials requires exclusion of atmospheric carbon dioxide during sample preparation, and maintenance of random orientation of powder samples (Copeland and Bragg, 1958).

The basis of quantitative estimation of calcium hydroxide formation in hydrating cement pastes by x-ray diffraction is the comparison of two major diffraction peaks, $2\theta=34°$ and $2\theta=18°$. Ratio of the peak intensities $I_{34°}/I_{18°}$ should be about 1.4. The amount of a given component (e.g., $Ca(OH)_{2(s)}$) in the cement matrix can be determined if a known amount of a standard compound (e.g., KBr with major peak at $2\theta=27.02°$) is added to the mixture prior to x-ray diffraction analysis (internal standard). A calibration curve can be constructed from a series of mixtures containing known amounts of the phase to be measured, according to the relationship

$$\frac{I_i}{I_s} = K\frac{M_i}{M_s}$$

where M_i = mass of mineral i

                 M_s = mass of standard mineral

                 I_i = intensity of reflections of mineral i

                 I_s = intensity of reflections of standard mineral

15

K — a constant dependent on characteristics of the apparatus and structure of component.

The intensities of the characteristic reflections are represented by the areas under diffractometer chart peaks.

Preparation of Samples for Calibration Curve and X-ray Analysis

Four different mixtures containing, respectively, 15%, 30%, 50%, and 66.7% (by weight) of $Ca(OH)_{2(s)}$ were prepared with KBr. Each solid was first ground separately to pass a 45 μ sieve. The aluminum sample holder was placed on a glass slide with a rough surface and fixed to it with adhesive tape. The hole was filled with the material to be studied and covered with another glass slide and compacted gently. More material was added, and likewise compacted. Fine glass powder was added during compaction to avoid preferred orientation of the sample.

Samples from specimens of hydrating cement paste and cement-clay mixtures were ground and prepared similarly, using KBr as internal standard.

Differential Scanning Calorimetry was performed with a cell supplied as a module to a Du Pont 990 thermal analysis system. Thermograms can be obtained from room temperature to 600°C. Heating rate for the 14 to 20 mg samples used in preliminary tests was 10°C/min, in an atmosphere of nitrogen gas.

Infrared spectrometry was also tested as an alternative method for identification of calcium hydroxide in hardened cement-clay mixtures. The method is based on absorbance of radiation within the infrared range by vibrations of particular groups of atoms in a molecule. The method is used primarily for organic molecules, but there are certain groups of inorganic compounds that vibrate in frequencies that absorb in the infrared range; for example, the OH bond exhibits a stretching vibration, as does the Si-O bond important in silicate

16

compounds. Polymorphs of dicalcium silicate, for example, have been identified using IR spectroscopy (Puertas and Trivino, 1985). The instrument used during the first year of this project was a Perkin Elmer 283 Infrared Spectrophotometer. Dry samples were prepared as mixtures with KBr by mulling in an agate mortar, followed by forming into a wafer by application of a pressure of about 9 tonnes.

Compressive Strength

Feasibility criterion for the clay-cement paste mixtures during the first year of work included comparison of the compressive strengths of the mixtures with values obtained with hardened cement pastes without the clay additives. Cement-clay mixtures in which 8% and 20% of the cement was replaced by the specific clay were used in these initial tests. Blending of the cement with clay was done by hand with a spatula in two steps: first, half of the amount of cement was mixed with half of the amount of clay; the procedure was repeated with the remaining halves, and the two blended mixtures then were combined. Water was then added to the mixture, and mixed by hand for 5 minutes. The water-to-(cement+clay) ratio was 0.6 in all the samples for feasibility testing, in order to obtain good workability.

Plastic molds for specimen forming were cylindrical: diameter = 1.9 cm (3/4 inch) and height of 7.62 cm (3 inches). The molds were stored in a humid chamber at 21°C (70°F) and 90% relative humidity, for 24 hours. The samples were removed from the molds and immersed in lime-saturated distilled water for periods of 7, 14, and 28 and 90 days. After this curing period, the specimens were ground at both ends to a height of 5.7 cm (2¼ inches). Compressive strength of the specimens were determined using a MTS machine with a 442 controller, a 410 digital function generator, and a load cell for 100 KN. Tests were run as stroke-controlled (4000 seconds for 10 v).

Clay Pretreatment

Experiments with cement-clay mixtures were done for cases in which the clays were used as received, and for cases in which the clays were pretreated to replace all counterions on exchangeable sites with H^+. This was done by leaching samples of the pure clays with 0.001M HCl under vacuum filtration, followed by removal of excess pore acid with isopropyl alcohol. The resulting H-clays were then air-dried and pulverized to pass 425 μ sieve.

Chemistry of Pore Fluid

In order to understand the physico-chemical processes taking place in hydrating mixtures of cement and clay, and to monitor chemical effects of the clay counterions on chemistry of the pore fluid, it is necessary to obtain samples of the fluid during the hydration process. An apparatus to extract fluid from hardened cement pastes has been described (Barneyback and Diamond, 1981). Based on that work, a specimen "squeezer" is being constructed to fit use with a high pressure apparatus in the Geological Sciences department. For analysis of the extracted pore liquid, an ion chromatograph (Dionex 4000i) was purchased, set up, calibrated, and tested. This instrument allows chemical speciation of ions in solution based on principles of ion exchange on resin columns, and detection of ions by electrical conductivity or wave length absorbance. Selection of the appropriate combination of resin column, eluting solution, and method of detection is somewhat of an art requiring experience with the particular solutions. The unit is now operating routinely for analysis of cement paste aqueous extracts for the most common alkali and alkaline earth cations, anions except for OH^- and carbonates (which are measured by titrimetry), and transition metals such as iron.

Degradation of Clay Additives

One of the uncertainties in results hypothesized for clay addition to cement pastes is the effect on clay structure of the high pH of the hydrating mixture. For example, it is well known that silica tends to be removed from aluminosilicate clays in high pH solutions (Grim, 1953). X-ray diffraction techniques are readily applicable to monitor quantitative loss of clay mineral crystal structure if an internal standard is included in the mixture.

RESULTS AND DISCUSSION

General Observations

Cement pastes containing 8% or 20% of the individual clay minerals kaolinite, bentonite, and attapulgite, maintained their integrity for experimental curing periods up to 90 days. Workability of the pastes during mixing, however, was more difficult than pastes prepared without the clays. Degree of workability decreased in the order kaolinite > attapulgite > bentonite. The high surface area due to the expanding lattice layers of bentonite, leading to larger proportions of bound water, may account for the poor workability of mixtures with this clay. In all cases, the water-solids ratio of 0.5-0.6, rather higher than would be desirable for high-strength materials, was used to allow good workability during the feasibility study. Eventually, a lower water:solids ratio is intended to be used, perhaps with the addition of superplasticizers.

Compressive Strength Tests

Results of initial tests on cement-clay mixtures (Table II) indicate that kaolinite did not significantly affect compressive strength of test cylinders compared to the reference specimens (cement paste w/o added clay). Test values for specimens containing bentonite clay were about 20% lower than the reference values.

Attapulgite, on the other hand, significantly increased compressive strength (by a factor of 2.6) for a mixture containing 8% clay but not at 20% clay. Tests with this clay are continuing.

Since porosimetric data for these specimens have not yet been obtained, conclusions regarding clay additive effects on pore size distribution as related to compressive strength cannot be made. Beaudoin has reported that microstructural effects of mica addition to Portland cement paste were dependent

20

Table II. COMPRESSIVE STRENGTH OF CEMENT-CLAY SPECIMENS (Water/solids = 0.6)

Mixture	% clay	Compressive Strength (MPa)
		After 28 days Hydration
Cement (Reference)	0	36.2 ± 0.0
Cement-Bentonite	8	26.9 ± 1.6
	20	29.0 ± 1.4
Cement-Kaolinite	8	33.8 ± 1.7
	20	32.8 ± 2.5
Cement-Attapulgite	8	93.5 ± 2.1
	20	37.5 ± 2.1

on water-cement ratio and amount of mica added. (Mica is a flakey-type clay mineral, unlike attapulgite which is needle-like). Beaudoin also found that mica addition generally retarded cement hydration (Beaudoin, 1986).

No significant differences were observed in compressive strength test values between specimens containing kaolinite and bentonite in their original state and when counterions were replaced with H^+ (Table III). Corresponding data for attapulgite has not yet been obtained.

21

Table III: COMPRESSIVE STRENGTH OF CEMENT-CLAY SPECIMENS: Untreated Versus H^+-clays water/solids = 0.6.

Mixture	% clay	Compressive Strength (MPa)	
		Untreated	H^+ Clay
After 7 days Hydration			
Cement (Reference)	0	16.0 ± 0.0	
Cement - Kaolinite	8	12.9 ± 0.4	14.7 ± 0.4
	20	17.5 ± 0.4	18.1 ± 1.3
Cement - Bentonite	8	18.4 ± 0.8	15.2 ± 1.7
	20	18.4 ± 0.0	16.4 ± 1.1
After 14 days Hydration			
Cement (Reference)	0	21.0 ± 1.4	
Cement - Kaolinite	8	26.0 ± 2.8	23.0 ± 0.0
	20	22.9 ± 0.1	22.9 ± 0.1
Cement - Bentonite	8	20.2 ± 1.1	21.7 ± 0.0
	20	20.0 ± 0.0	20.0 ± 1.7

Calcium Hydroxide Quantitation

Calibration of X-ray diffraction data for $Ca(OH)_{2(s)}$ quantitation are shown in Fig. 2. Application of the calibration curve to hydrating cement paste and hydrating cement-clay paste samples, however, was not successful. In no case were the intensities of the $Ca(OH)_{2(s)}$ peaks ($I_{18^\circ}/I_{34^\circ}$) equal to 0.74. For example, in the reference sample (hydrating cement only), ($I_{34^\circ}/I_{18^\circ} \approx 1$). On the assumption that perhaps random orientation was not achieved, various proportions of ground glass were used, without success. Recent work by Zurz and Odler reported similar difficulties. These authors suggested that orientation of the portlandite crystals may not be the only reason for an increased $I_{(001)}/I_{(101)}$ peak ratio (compared to the desired 0.74 orientation index); rather, variation in peak
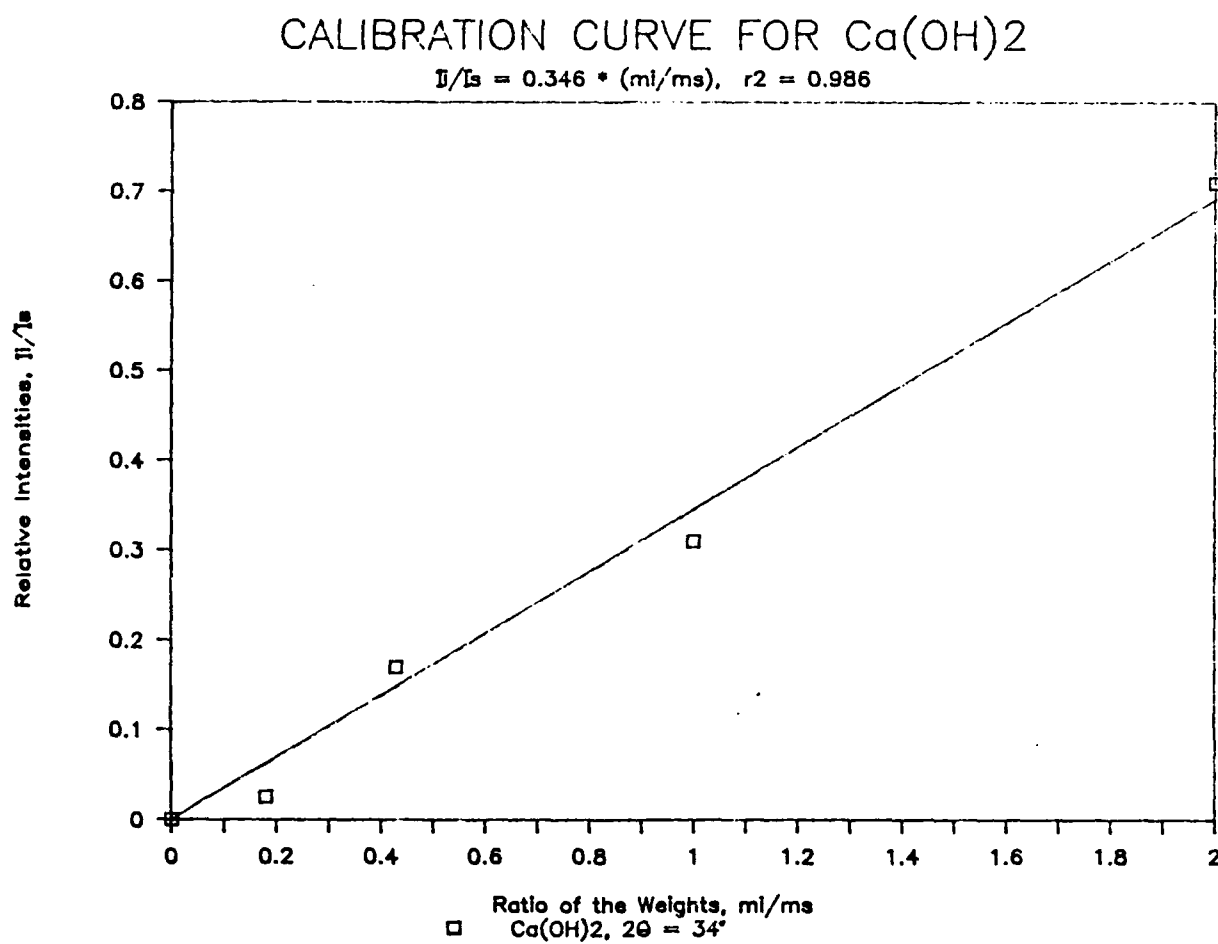
CALIBRATION CURVE FOR Ca(OH)2

$I_l/I_s = 0.346 * (m_l/m_s)$, $r2 = 0.986$

Figure 2. Calibration Curve for Ca(OH)$_{2(s)}$ Obtained from X-Ray Diffraction Data of Mixtures with KBr.

intensity ratios may be related to changes in the morphology of the portlandite crystals formed (Zurz and dOdler, 1987).

Until this problem can be resolved, alternative methods for quantitative determination of $Ca(OH)_{2(s)}$ in hydrating cement pastes become important to investigate, as supplementary or confirmatory, to x-ray diffraction techniques. One such alternative method is differential scanning calorimetry.

<u>Differential scanning calorimetry</u> is an alternative method applied to calcium hydroxide quantitation. Thermograms obtained with mixtures of reagent-grade calcium hydroxide and portland cement (Fig. 3) indicate promise for quantitation of calcium hydroxide even for non-crystalline solid phases. An important question still under investigation is whether in hydrating mixtures of cement and clay there may be endothermic peaks due to other solid phases at around 500°C. If so, such compounds would interfere with analysis for $Ca(OH)_2$. Initial results indicate that the clay mineral attapulgite has a single endothermic peak at about 200°C, and thus should not interfere with calcium hydroxide measurement in mixtures.

Pore Fluid Chemistry

Examples of the output from the ion chromatograph are shown in Figs. 4a and 4b. Samples were 50 μl each of solutions extracted from hydrating mixtures of cement and clay for analysis of alkali and alkaline earth cations. Due to the large differences in concentrations of certain cations (calcium and magnesium, for example) in the pore fluid it is not possible to obtain all the desired cationic concentrations from a single injection of sample; (hence the negative sign for magnesium in Fig. 4). Rather, several injections at appropriate dilutions are necessary. All solutions injected into the ion
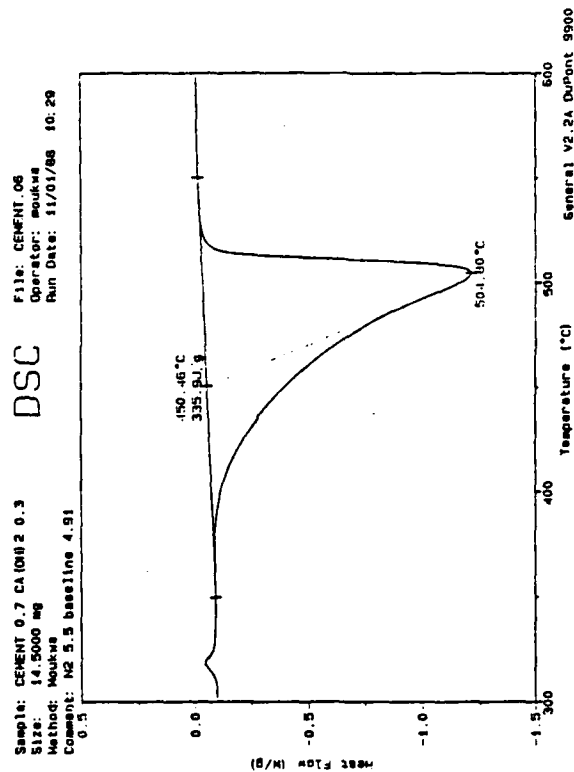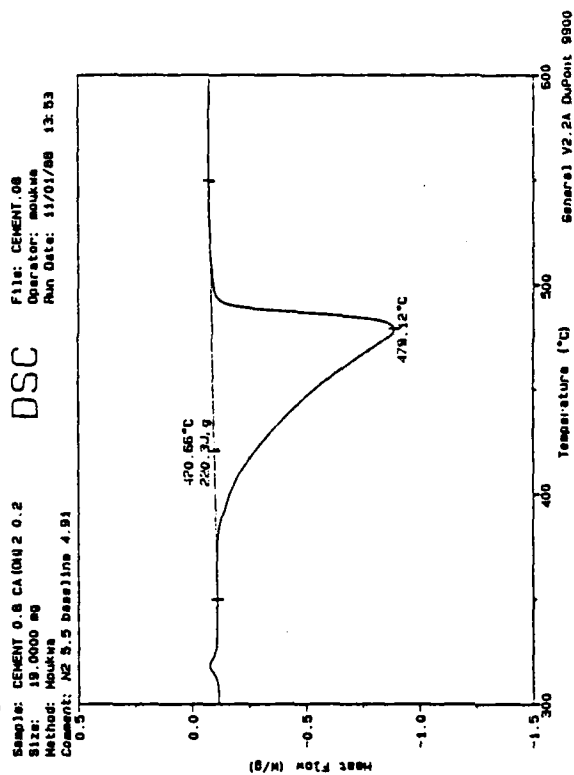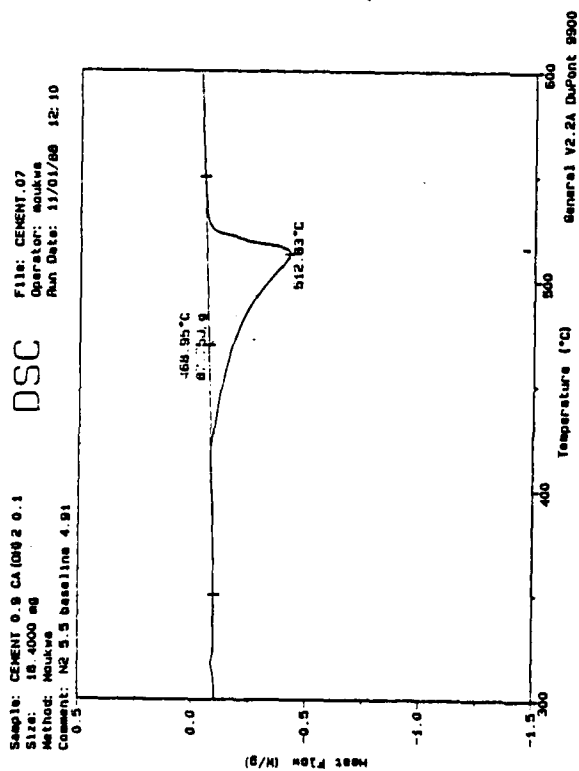
24

Figure 3. Thermograms of Reagent-grade

$Ca(OH)_{2(s)}$ in Portland Cement Mixtures

at 10-, 20-, and 30% $Ca(OH)_2$, respectively.

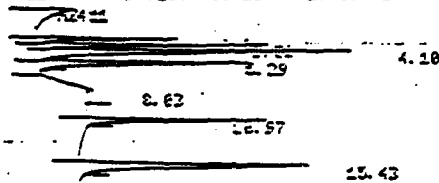ALKALI METALS + ALK EARTH   06/12/88 16:41:21   CH= "A" PS= 1

FILE 0.   METHOD 5.   RUN 8   INDEX 2

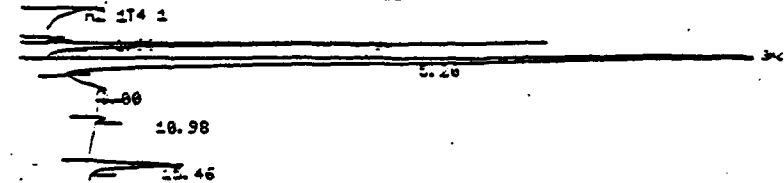ANALYST: EKG

SAMPLE 2   CEMENT 0% 1hr

SR	IS	XF
0.	0.	50.

NAME	PPM	RT	AREA BC	RF	RRT
LI	18.227	2.94	784899 01	76572.887	1
NA	498.767	3.52	16219874 01	33726.437	1
K	2476.274	5.11	76485494 01	30887.521	1
4	0.	6.83	2611762 01		0.721
MG	-1.286	10.98	415280 01	1	
CA	492.888	15.42	22521537 01	45755.46	1

TOTALS   3476.25   116258846

(a)

CHANNEL A   INJECT 06/12/88 16:59:21

4.10
3.29
6.83
10.97
15.43

ALKALI METALS + ALK EARTH   06/12/88 16:59:21   CH= "A" PS= 1

(b)

CHANNEL A   INJECT 06/12/88 17:53:21

5.20
10.98
15.46

ALKALI METALS + ALK EARTH   06/12/88 17:53:21   CH= "A" PS= 1

FILE 0.   METHOD 5.   RUN 12   INDEX 1

ANALYST: EKG

SAMPLE 2   CEMENT 8% 1hr

SR	IS	XF
0.	0.	50.

NAME	PPM	RT	AREA BC	RF	RRT
LI	6.166	2.9	464383 01	75288.518	1
NA	518.668	3.53	17641689 01	33856.642	1
K	2553.927	5.2	78687222 01	30252.584	1
4	0.	6.	3067989 01		0.729
MG	-1.599	10.98	283047 01	1	
CA	38.572	15.46	6571196 01	222852.866	1

TOTALS   2888.134   98445546

Figure 4.   Ion Chromatograms of Solutions Extracted from (a) hydrating cement paste (1:50 dilution), and (b) hydrating cement-clay (8%) mixture (1:50 dilution, after 1 hour.   Note decrease in Ca concentration (a) to (b).

26

chromatograph are filtered through a 0.22 μm filter, which in essence, defines the "soluble" species.

Using a clay-cement mixture containing 8% untreated kaolinite, with a water:solids ratio of 0.5, pore solution was extracted after the mixtures had stood for 5 minutes, and again after 1 hour. As shown in Figs. 4a and 4b, calcium ions were essentially removed from solution after 1 hour, in the presence of kaolinite (about 30 ppm Ca^{+2} remaining); in the absence of kaolinite, about 500 ppm calcium was in solution after 1 hour. The clay appeared to have little effect on removal of monovalent cations from solution. It can not be ascertained at this point whether removal of the calcium ions was an adsorption phenomenon or an acceleration of precipitation phenomena. This is an important aspect of clay-cement interaction that continues to be investigated. Calcium removal from solution in the presence of kaolinite was not consistently obtained, indicating that this phenomenon, if it is real, will require investigation under better controlled conditions than those of these initial trials.

At least two questions on the application of ion chromatography to cement paste pore liquid analysis needed immediate resolution:

(1)   Would the time interval between mixing of the cement and water, and extraction of the pore liquid, be a large factor in the analysis?

(2)   Would the time interval between extraction of the pore liquid, and analysis be a factor in the analytical results?

Table IV lists results of tests with hydrating mixtures of cement, cement + kaolinite clay (8%), and cement + treated kaolinite clay (8%), at water:solids ratios of 0.5. Pore liquid was extracted by vacuum filtration through 0.22 μ filter 5 minutes after mixing, and 60 minutes after mixing. Aliquots of the solutions were taken for analysis by ion chromatography, and the remaining

Table IV: EFFECT OF TIME INTERVAL (5 OR 60 MINUTES) BETWEEN SOLIDS MIXING AND PORE SOLUTION EXTRACTION ON THE CONCENTRATIONS OF MAJOR IONS IN PORE FLUID AS MEASURED BY ION CHROMATOGRAPHY ON THE SAME DAY, AND 6 MONTHS LATER (Water/Solids = 0.5).

Percent Kaolinite in Mixture	0		0		8		8		8T*		8T*	
Day of Analysis	Same Day		+ 6 Mos.		Same Day		+ 6 Mos.		Same Day		+ 6 Mos.	
Time Interval (minutes)	5	60	5	60	5	60	5	60	5	60	5	60
Cations (mg/liter)												
Na^+	480	486	460	450	417	431	360	400	437	448	390	400
K^+	3140	3170	3200	3200	2250	2300	2500	2500	2400	2476	2700	2800
Ca^+	836	851	670	640	866	780	837	720	808	792	550	630
Anions (mg/liter)												
SO_4^{-2}	3770	2930	3600	2800	2490	2900	3140	2400	3390	2680	3200	2500
Cl^-	163	187	152	177	172	120	130	151	148	180	145	173

* 8T = 8% Treated clay (adsorbed ions replaced with H^+).

portions stored at room temperature in capped vials. There was no attempt to exclude atmospheric carbon dioxide from the vials. After 6 months, aliquots were again taken from the vials and analyzed by ion chromatography.

Dilutions of the aliquots were necessary (1:50 to 1:250) just prior to injection into the chromatographic column, as the pore solutions were much too concentrated for direct injection. All values in Table 4 have been corrected for dilution.

Values in Table IV are the means of duplicate analysis; errors for K, Ca, sulfate and chloride are on the order of 1-3%; values for Na, however, have errors up to 30%, due mainly to the fact that at the dilutions taken, the Na peak occurs very close to the point of a dip in the baseline due to water. This problem can be remedied by analyzing for Na separately if necessary, using much greater dilutions such that the Na peak separates farther down on the column, thus avoiding the water dip.

Inspection of Table 4 data indicate that Na^+, K^+, and Cl^- data were not appreciably affected by the indicated time intervals. Ca^{+2} and SO_4^{-2} values, however, tended to decrease over the 6-month storage interval, probably due to precipitation in the solution of calcium carbonate, calcium sulfate, and/or calcium hydroxide. White particles were observed to have settled out on the sides of the capped vials.

Sulfate ion concentrations in the extracted liquid tended to be significantly lower after the 1-hour interval between mixing and extraction than after the 5 minute interval. Since the Ca^{+2} did not appear to decrease correspondingly, it is suggested that the sulfate was precipitating out in the hydrating mixture with some other ion than was measured here; one such cation, for example, is aluminum with the possible formation of ettringite. Analysis

29

for Al ion by ion chromatography requires use of a different resin column and eluant than was available at the time. Analysis for this ion, and its various forms in the pore liquid, is important in terms of Al released by clays into solution, as well as for the formation of ettringite. This work is continuing.

Clay Degradation

Inspection of x-ray diffraction peak intensities from XRD analysis of a 30% kaolinite-cement mixture (0.5 water:solids ratio) that had been cured for 7 days, indicated that the kaolinite may have undergone crystal lattice degradation. As discussed briefly above (TECHNICAL BACKGROUND), the high pH of the pore solution during hydration is expected to dissolve some silica from the clay lattices. (Pore solutions extracted after 7 to 14 days curing were at pH values of about 11.3 to 11.8). It is important to determine whether such degradation will lead to a reduction in porosity due to positioning of degradation products (e.g., colloidal silica and alumina) in pores, and what effect the phenomena will have on mechanical properties of the hardened pastes. Procurement of a mercury intrusion porosimeter early in the project's 2nd year will help to resolve these uncertainties.

CONCLUSIONS

The first year on the project was spent primarily in development of methods for use in the study of the physical chemistry of Portland cement to which alumino-silicate clays are added, with the aim of improving strength, durability, and toughness of cement-based composites. Quantitative monitoring of calcium hydroxide phases in the hydrating mixtures is essential to developing an understanding of the manner in which chemistry of the material affects mechanical properties. To this end, quantitative x-ray diffraction using an internal standard and relative peak intensities is under investigation. Results to date indicate that the major interferences and difficulties with this method appear to arise from possible changes in the crystal morphology of the calcium hydroxide solid phase in the hydrating mixtures, as well as the usual problem of non-random orientation in such samples. Maintenance of a CO_2-free atmosphere during sample preparation appears to be important. An alternative method that may supplement x-ray diffraction, particularly in cases of amorphous material, is differential scanning calorimetry. Initial efforts at developing a calibration technique appear fruitful.

Of the three representative clay minerals investigated so far, attapulgite (palygorskite) seems to hold the greatest promise for increasing compressive strength of cement pastes. Porosimetric data are essential to defining the microstructure effects of the needle-like morphology of palygorskite compared to the platey morphology of kaolinite and bentonite.

Modification of pore solution chemistry by addition of clays whose exchange sites are saturated with a specific ion does not appear to be significant at 8% clay (proportion of the cement replaced by clay). Studies with clay additions of 20% or more are continuing.

31

There was some evidence that the kaolinite crystal lattice degradation occurred during cement hydration. Kinetics of the reaction, and effects of clay degradation products on porosity and mechanical properties of hardened pastes, are to be investigated during the project's second year.

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